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(19) (CA) **CANADIAN PATENT** (12)

(54) Process for the Controlled Production of Silica  
by Means of Flame Hydrolysis

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The present invention relates to the production of silica and in particular to the production of silica by flame hydrolysis.

The production of silica by pyrogenic means, for example, by subjecting silicon tetrachloride to a flame hydrolysis is known. These kinds of silica are, for example, the different silica types marketed under the name of Aerosil®. They have varying particle sizes ranging from 7 to 40 nm and, therefore can be used in greatly varying fields of application, as for example  
10 for the thickening of liquid systems.

The specific surface area, measured in sq m per gram according to BET (not the particle size) is usually used as the typical characteristic quantity. Insofar as silicas free from pores are concerned these two quantities are closely correlated.

A characteristic which is just as important is the thickening effect of the different silica types in a liquid system, since most of these silica types are used as thickening and thixotropic agents. This characteristic is a function of the BET surface area so that in conventional silica types which are produced  
20 by means of a flame hydrolysis a specific thickening effect can also be attributed to a specific surface area.

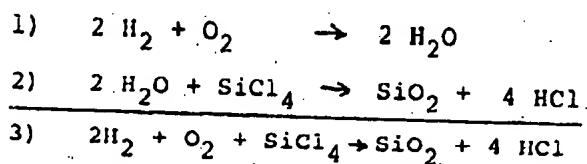
This kind of correlation is shown graphically in Figure 1 of the accompanying drawings, in which:-

Figure 1 shows the thickening effect as a function of the BET surface area for conventional silicas;

Figure 2 shows the thickening effect as a function of the quantity of added water vapour in correlation to the BET surface area for silicas produced by means of the process according to the invention when the additional water vapour is passed in-  
30 to the reaction mixture before reaching the combustion chamber;  
and

Figure 3 shows the thickening effect as a function of the quantity of added water vapour in correlation to the BET surface area for silicas produced by means of the process according to the invention when the additional water vapour is fed into the flame.

In the known processes of flame hydrolysis of silicon halogen compounds in a hydrogen flame using the hydrolysis of silicon tetrachloride-air or oxygen as an example, hydrogen and silicon tetrachloride are mixed with one another and burned off in such a ratio that the hydrogen can burn completely while forming water vapour and that the silicon tetrachloride can react quantitatively with the water vapour formed while forming  $\text{SiO}_2$ . The reactions which proceed consecutively and concurrently can be represented by the equations 1, 2 and 3:



These equations are also applicable when other silicon halogen compounds are used as starting substances. For this purpose vaporizable inorganic halogen compounds and/or organic halogen compounds of silicon are used. For example  $\text{SiHCl}_3$ ,  $\text{SiCl}_2\text{H}_2$  or  $\text{SiCl}_4$  are useful as inorganic halogen compounds and  $\text{CH}_3\text{SiCl}_3$ ,  $(\text{CH}_3)_2\text{SiCl}_2$ ,  $(\text{CH}_3)_3\text{SiCl}$ ,  $\text{CH}_3\text{-CH}_2\text{-SiCl}_3$  or  $(\text{CH}_3\text{-CH}_2)_3\text{SiCl}_2$  as organic halogen compounds.

For carrying out the combustion hydrolysis the components hydrogen, oxygen or air and silicon tetrachloride are fed, either separately or premixed, to a type of burner such as that shown diagrammatically in the US Patent 2,990,249. The quantity of hydrogen is so calculated that, during the formation of water vapour, it is sufficient for a quantitative reaction of the chlorine atoms on the silicon atom while forming hydrogen chloride. A slight excess assures that the reaction proceeds not only

quantitatively but also exceedingly fast. It is not possible to use an arbitrarily high excess of hydrogen, relative to the amount of silicon tetrachloride. Quite apart from the fact that this measure would unnecessarily increase the costs of the process, the hydrogen excess is limited in that not only does this reaction component constitute the component required for the hydrolysis of the chloride but it also supplies the energy. If the increase of the hydrogen excess is too large, the effect would be that the temperature of the flame rises with unfavourable consequences for the quality of the  $\text{SiO}_2$  reaction products. It is also possible to reduce the reaction temperature by adding quantities of air or oxygen which exceed the stoichiometric amount. With this measure the reaction temperature is usually influenced and the fine division or the specific surface area of the reaction products thus is fixed. However, this possibility is limited since the discharge velocity from the burner orifice must move within relatively narrow limits and the increase of the quantity of inert gas is at the expense of the performance of the apparatus.

The known process for producing silicas by means of flame hydrolysis according to the US Patent 2,990,249 has the disadvantage that it is not possible therewith to change the correlation between specific surface area and thickening pattern and to adjust the thickening effect of the silica independently of the value of the specific surface area.

The present invention provides a process for the controlled production of silica by means of flame hydrolysis, characterized in that additional amounts of water vapour, which do not result from the combustion of hydrogen or of hydrogen-containing gases required for the flame hydrolysis, are introduced into the reaction mixture.

The introduction of the additional water vapour can be

carried out in various ways. Thus, the additional water vapour can be passed into the mixing chamber of the burner via a separate conduit. In another preferred embodiment of the process according to the invention the additional water vapour may be fed into the hydrogen or air supply to the burner whereby a mixture of hydrogen and water vapour or a mixture of air and water vapour is fed to the burner. For the mixing with water vapour the hydrogen or the oxygen-containing gas may be passed through a water evaporator at a temperature ranging from 20°C  
10 to the boiling temperature of the water.

In a further preferred embodiment the additional water vapour can be admixed with the chloro silicon compound before the latter compound enters the burner. However, the temperature of the mixture from chloro silicon compound must be kept above the dew point in order to avoid separation of silica.

In yet another embodiment of the process according to the invention the additional water vapour can also be fed into the flame, the region of the actual silica formation. This can be done by means of a lance, which is passed axially through the  
20 burner and is allowed to project from the burner orifice. However, it is important that the mixing procedure is as fast and homogeneous as possible so that the influence of the additional water vapour on the occurrence of the reaction and on the formation of the silica can be fully effective since the influence of the partial pressure of the water vapour decreases with the distance from the burner orifice. At the outlet of the so-called flame tube, i.e. a heat exchanger zone, into which the flame gases are usually injected no influence on the formation of properties of the silica upon admixing additional quantities of  
30 water vapour is detectable.

The admixed quantity of water vapour may be varied within wide limits.

The water vapour is preferably added at a temperature from 150 to 250°C and at an excess pressure of 10 to 20 atmospheres, particularly at a temperature from 185 to 210°C and at an excess pressure of 12 to 18 atmospheres.

Any known inorganic<sup>chloro</sup> and/or organic silicon halogen compound can be used as the starting substance.

The ratio of water vapour to starting substance may be from 0.1 to 1 kg of water vapour per kg of starting substance.

10 In a further embodiment of the invention, e.g. a hydrocarbon, instead of pure hydrogen, may be used as the burner gas. These hydrocarbons may be for example, propane and/or butane.

An apparatus like that described in the US Patent 2,990,249 can be used as the burner. However, a closed burner system, in which no secondary air can penetrate the flame, may also be used.

The controllability of the thickening effect is evident from the accompanying drawings.

20 According to Figure 1 the thickening effect as a function of the BET surface area is shown graphically for silicas produced by means of conventional processes. The following values are obtained for the individual silicas:

surface area	thickening
130 sq m/g	2000 mPas
150 sq m/g	2700 mPas
200 sq m/g	3100 mPas
300 sq m/g	3500 mPas
380 sq m/g	3000 mPas

These thickening values were determined from a polyester reference system.

30 This polyester reference system is produced by mixing 80 parts by weight of Ludopal P6 (a trademark) with 11.4 parts by weight of monostyrene and 7 parts by weight of styrene con-

taining 1 part by weight of paraffin. This system is also used in all the further determinations of the thickening.

According to Figure 2 the entire pattern of properties, particularly the specific surface area and the thickening pattern of the silicas obtained shifts as the amount of water vapour added increases.

10 The curve a) thus shows the correlation between the specific BET surface area and the thickening pattern of silicas obtained by means of conventional processes by varying the excess of air. Thus, this measure makes it possible only to attain the combination of properties of the silicas shown in Figure 1.

However it is evident from the curve b) that as the addition of water vapour to the reaction mixture prior to the combustion increases both the thickening pattern and the specific BET surface area first extend far beyond the values known from the conventional silicas according to the curve a) whereupon they substantially decrease with larger quantities of water vapour and new combinations of properties are attained.

20 For example, it is thus possible to produce silicas having identical BET surface areas but greatly varying patterns of thickening.

According to Figure 3 the entire pattern of properties of the silicas obtained, particularly the specific BET surface area and the pattern of thickening, shifts as the quantity of water vapour added increases.

30 Thus, the curve a) shows the correlation between specific BET surface area and the pattern of thickening in silicas obtained by means of conventional processes by varying the excess of air. Thus, this measure makes it possible (as shown in Fig. 1 and 2) to attain only a combination of properties in which the thickening effect is a function of the specific BET surface area.

However, it is evident from the curve b) that as the addition of water vapour to the flame increases both the pattern of thickening and the specific BET surface area of the silicas obtained by means of the process according to the invention follow a path which differs completely from that of the curve a) corresponding to the known silicas, as compared with a basic standard. New combinations of properties can thus be attained.

For example, it is thus possible to produce silicas having identical BET surface areas but greatly varying patterns of thickening.

The process according to the invention is further described by way of the following Examples.

Example 1

6.2 kg of silicon tetrachloride are evaporated and mixed with 2.2 cu m of hydrogen and 5.8 cu m of air in the mixing chamber of a burner. The gas mixture burns from the outlet and is sucked into the cooling system by means of vacuum. After separation from the hydrogen chloride-containing gas mixture 2.2 kg of a highly dispersed silica having a specific surface area of 200 sq m per gram and a thickening of a polyester reference system of 3100 mpascals is obtained.

Example 2

The same procedure as in Example 1 is followed, but in addition to the substances mentioned therein, 0.5 kg of water vapour per hour is injected into the mixing chamber of the burner. The silica obtained has a specific surface of 466 sq m and a thickening value of 3910 mpascals.

Example 3

The same procedure as in Example 1, is followed by 1.8 kg of water vapour per hour are additionally added in the manner described in Example 2. The silica has a surface area of 277 sq m per gram and a thickening value of 1040 mpascals.



Example 4

The same procedure as in Example 1 is followed, but 0.5 kg of water vapour per hour is injected with a probe into the flame axis at a distance of 1 cm from the burner orifice. The silica has a specific surface of 309 sq m per gram and a thickening value of 4040 mpascals.

Example 5

10 The same procedure is followed as in Example 1 but with the difference that 3 kg of water vapour are injected into the flame axis at a distance of 10 cm from the burner orifice. The BET surface area of the silica is 212 sq per gram and the thickening value 1105 mpascals.

The values obtained in the above examples of the process according to the invention have been listed in Table I.

The values for the specific surface area and for the thickening correspond to the curves b) in Figure 2 and 3.

20

30

TABLE 1

Process according to the invention with additional injection of water vapour  
 a) into the reaction mixture prior to the combustion,  
 b) into the aerosil flame

operating conditions			injection of water vapors	surface area	thickening	thickening relative to standard
SiCl <sub>4</sub> kg/h	H <sub>2</sub> m <sup>3</sup> /h	air m <sup>3</sup> /h	kg/h	m <sup>2</sup> /g	m Pascal	%
a) into the reaction mixture prior to the combustion						
6.2	2.2	5.8	1.2	391	2215	76
6.2	2.2	5.8	1.8	277	1040	36
6.2	2.2	5.8	0.8	441	2865	99
6.2	2.2	5.8	0.5	466	3910	135
6.2	2.2	5.8	0.2	226	3255	112
6.2	2.2	5.8	0.1	214	3060	106
6.2	2.2	5.8	0.02	196	3060	106
b) into the aerosil flame						
6.2	2.2	5.6	0.8	348	3125	108
6.2	2.2	5.6	2.0	308	1605	58
6.2	2.2	5.6	3.0	212	1105	38
6.2	2.2	5.6	0.5	309	4040	139

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

C 1. In the production of silica by flame hydrolysis of a chloro silicon compound, a process for changing the correlation of specific surface and thickening characteristics, the thickening effect of the silica being adjusted independently of the value of the specific surface, the improvement in which ~~the~~ additional amounts of water vapour which do not result from the combustion of hydrogen required for the flame hydrolysis are fed into the reaction mixture and the mixing operation is carried out as rapidly and homogeneously as possible so that the influence of the additional water vapour on the reaction and the formation of silica is fully effective.

2. A process as claimed in Claim 1 in which the additional water vapour is passed into a mixing chamber of a burner with which the flame hydrolysis is effected.

3. A process as claimed in Claim 1 in which the additional water vapour is fed to a hydrogen or air supply in a burner effecting the flame hydrolysis.

4. A process as claimed in Claim 1 in which the additional water vapour is admixed with reactant chloro silicon compound in the flame hydrolysis fed to a burner.

5. A process as claimed in Claim 1 in which the additional water vapour is fed to the flame of the flame hydrolysis and into the hydrolysis region.

6. A process as claimed in Claim 5 in which the additional water vapour is fed axially into the flame by means of a lance.

7. A process as claimed in Claim 1, 2 or 3 in which the additional water vapour is added at a temperature from 150°C to 250°C at an excess pressure of 10 to 20 atmospheres.

8. A process as claimed in Claim 1, 2 or 3 in which the additional water vapour is added at a temperature from 185°C

to 210°C at an excess pressure of 12 to 18 atmospheres.

C 9. A process as claimed in Claim 1, 2 or 3 in which the flame hydrolysis is effected on a halogen silicon compound selected from  $\text{SiHCl}_3$ ,  $\text{SiCl}_2\text{H}_2$  <sup>and</sup> ~~or~~  $\text{SiCl}_4$ .

10. A process as claimed in Claim 1, 2 or 3 in which the flame hydrolysis is effected on a chloro silicon compound selected from  $\text{CH}_3\text{SiCl}_3$ ,  $(\text{CH}_3)_2\text{SiCl}_2$ ,  $(\text{CH}_3)_3\text{SiCl}$ ,  $\text{CH}_3\text{-CH}_2\text{-SiCl}_3$  <sup>and</sup> ~~or~~  $(\text{CH}_3\text{-CH}_2)_3\text{SiCl}_2$ .

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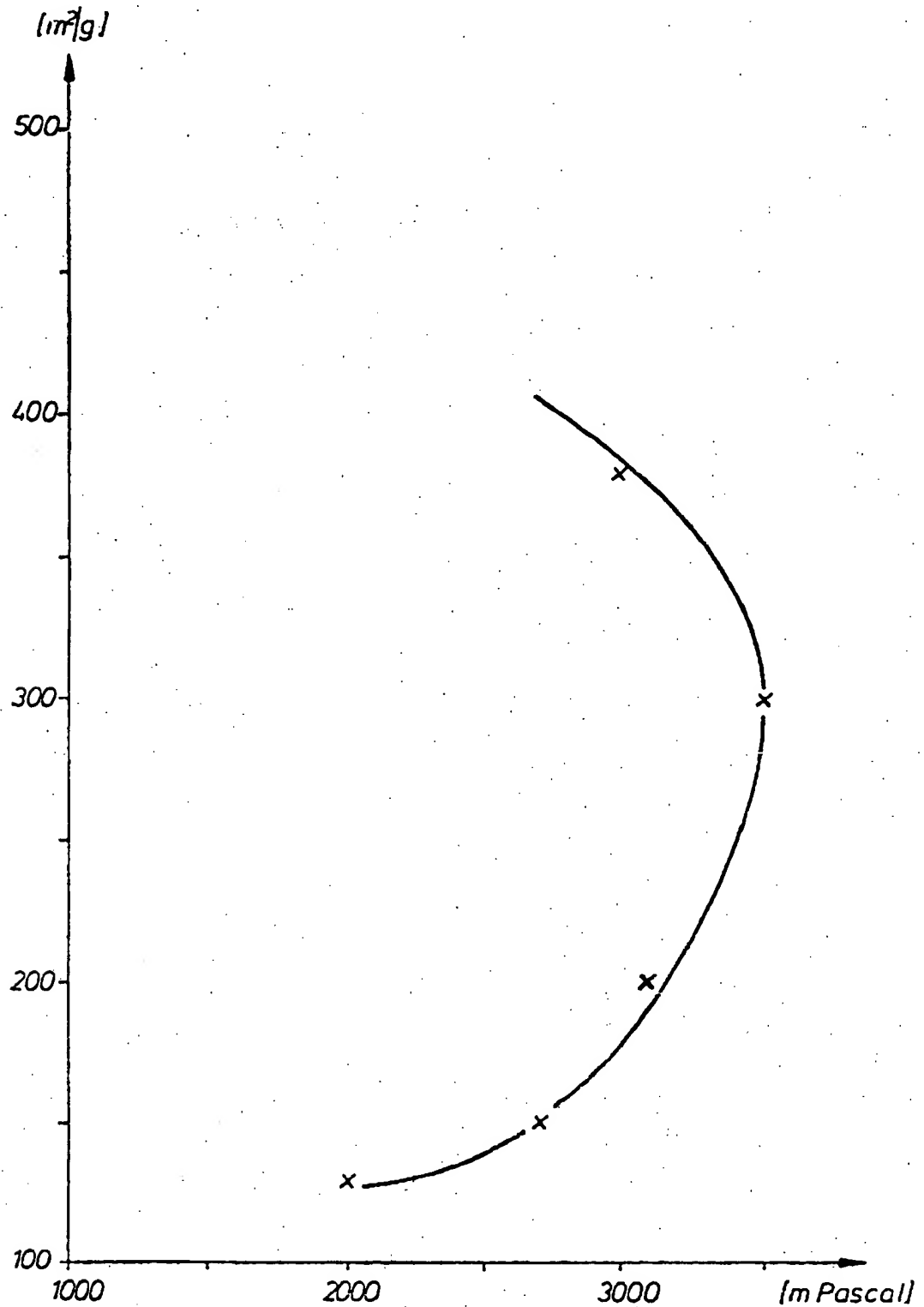


FIG. 1

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3.2

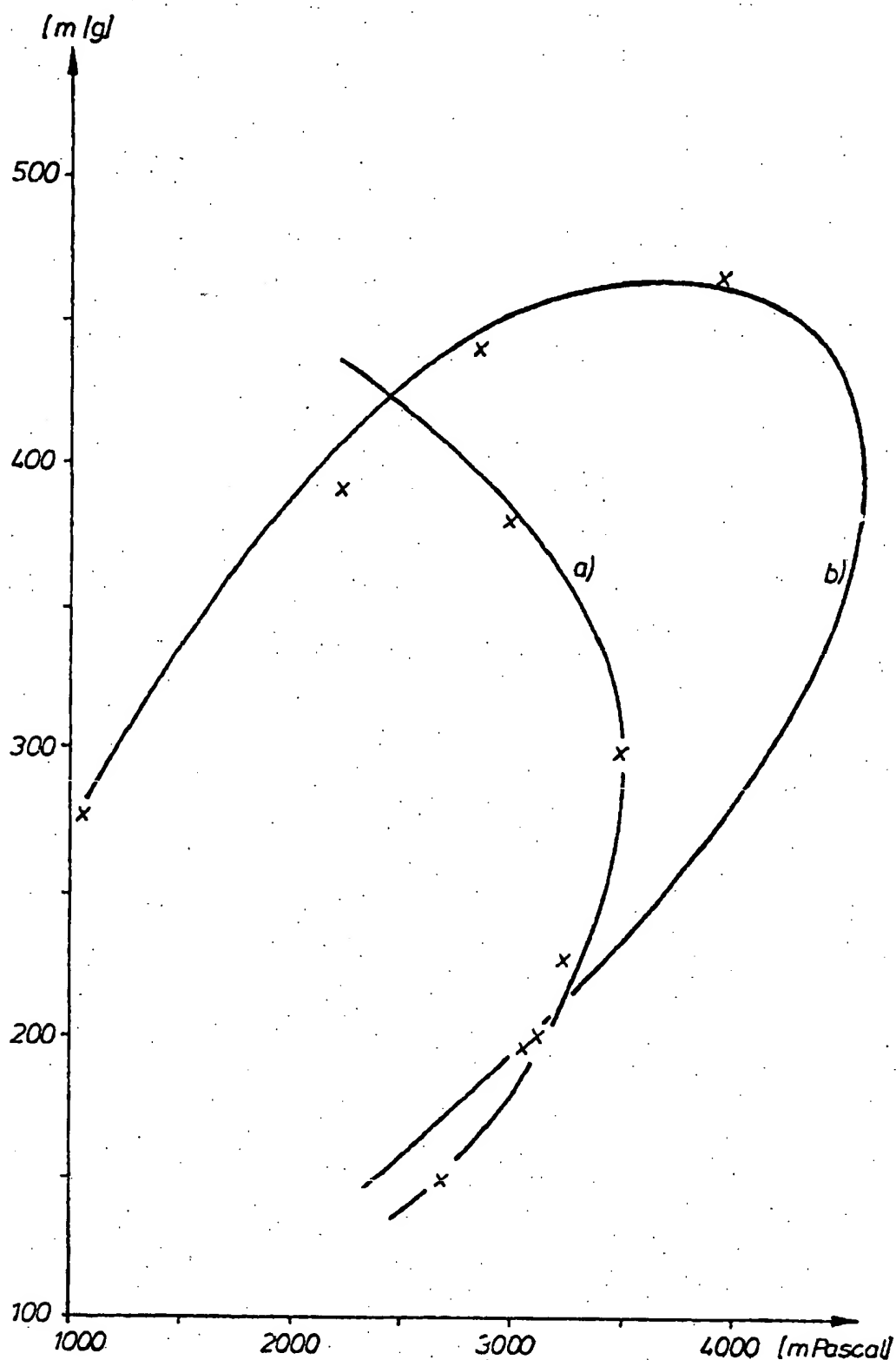


FIG. 2

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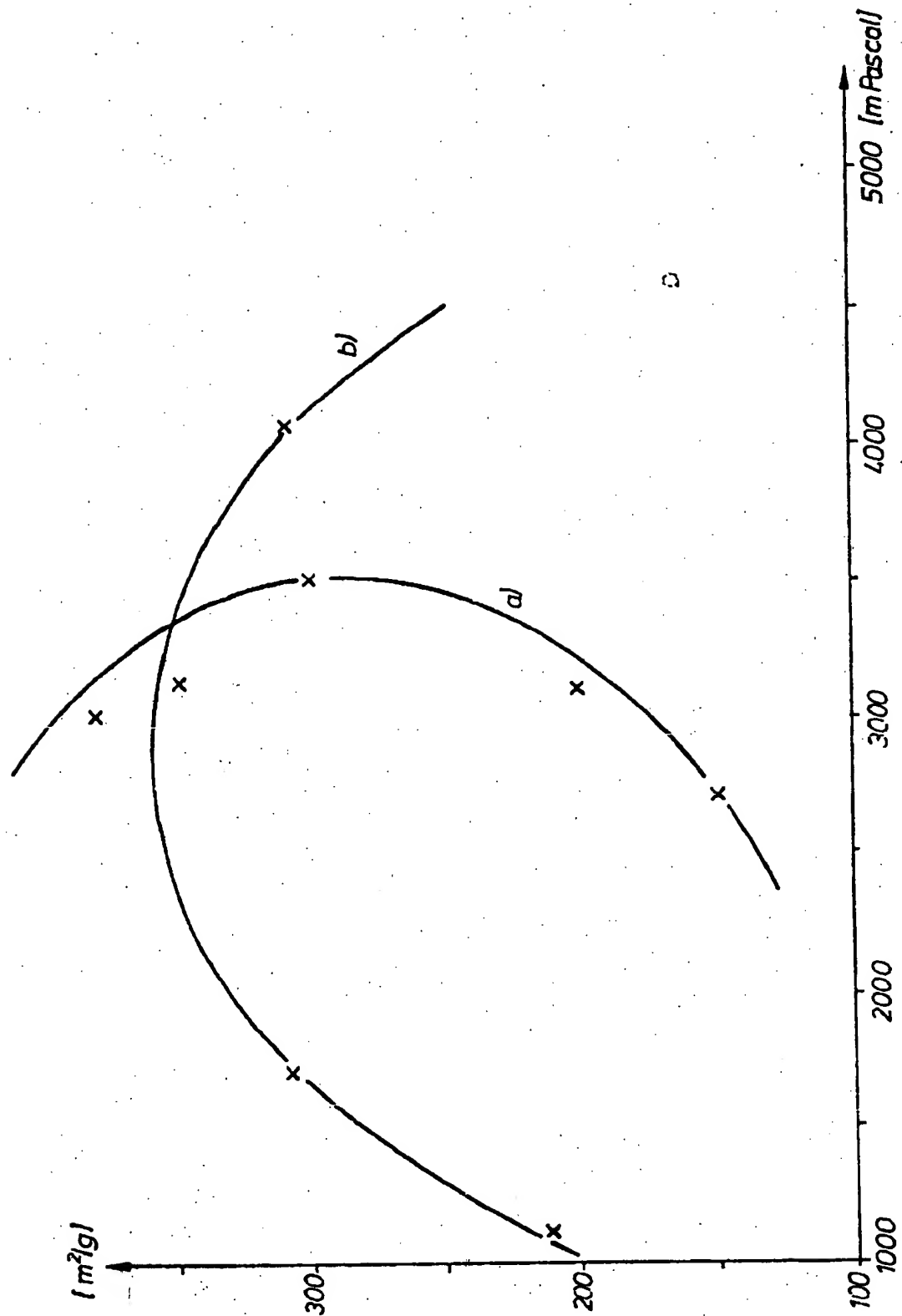


FIG. 3